NANOSTRUCTURED COATINGS ON FIRED GLAZES BY SPRAY PYROLYSIS

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ABSTRACT

This study investigated the deposition by the spray pyrolysis technique of nanostructured films on fired, glazed ceramic tiles, using the heat contained in the tiles as they crossed through the cooling section of their firing cycle, so that no additional energy contribution was required. The study examined, in particular, the effect of different variables (type of glaze, application temperature, precursor concentration, and type of deposited oxide) on the change in glaze appearance (colour and gloss), in order to evaluate the decorative possibilities of the technique.

Using copper or cobalt nitrates as precursors, which decompose at the operating temperatures used (400ºC–550ºC), the applied films altered the appearance of the tile in various ways, depending on the operating conditions used. The most notable change took place in the gloss: under optimum conditions, the gloss of the original glaze tripled. However, the application could also change the colour of the substrate completely or produce metallised effects.

The deposited films were made up of nanometric crystals, bonded to each other and to the substrate, though they did not form a continuous sheet on the fired glaze.

1. INTRODUCTION

Thin film technology has revolutionised the materials world in the last 30 years, as it has enabled energy and minerals resources be rationalised owing to the reduction in layer thickness, going from coatings of great thickness to thin surface films. Thin film deposition is currently one of the nanotechnology fields with the greatest practical applications, both in developing materials with new properties and in modifying traditional materials. A nanometre-thick layer of material behaves differently from the same material in massive form owing to the nature of the bonds in the layer, layer microstructure, and the morphology of the nanocrystals, layer microstructure and nanocrystal morphology depending on the technique used to produce the layer.[1]

Recently, the deposition of very thin or nanometric films on different materials (such as metals, polymers, and ceramics) has provided new applications as a result of the modification of surface properties.[2] The deposition of a nanometric layer of a given material on a substrate allows product properties to be enhanced and product functionality even to be changed: for example, coatings on steels to make them more wear resistant, or coatings that provide plastics with a metallic appearance.[3-5]

A similar technique is currently used in the ceramic industry in a limited way, involving the use of organic solvents, which may be organochlorates or alcohols. In both cases, very strict safety measures are required to avoid possible occupational and/or environmental accidents. It was therefore of interest to investigate the possibility of using aqueous precursors.

Spray pyrolysis has been one of the most widely used techniques in the last three decades for depositing a wide range of materials as thin films.[6] The simplicity of the apparatus used and the possibility of scaling up this technique have made it a very attractive route for the thin-film deposition of noble metals, metallic oxides, mixed oxides, compounds deriving from chalcogens, and superconducting compounds.[7-13]

In the deposition process, a precursor (solution or colloidal dispersion) is nebulised using a gas, so that it reaches the hot substrate in the form of very fine drops. After the solvent has evaporated, the reagents that are present react, forming the desired compound on the surface of the substrate and anchoring it to the surface.

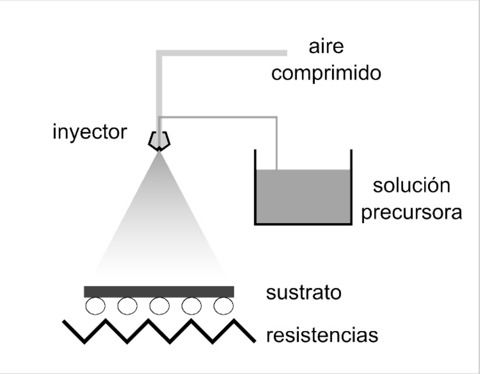

Figure 1. Basic scheme of the spray pyrolysis technique.

The typical scheme of a spray pyrolysis system (Figure 1) consists of an injector, a liquid precursor, a system for heating the substrate, a temperature control system, and a gas impeller (air compressor). The properties of the film deposited on the substrate depend, at least in principle, on the precursor composition, spray flow rate of the solution, substrate temperature, carrier gas, size of the deposited drops, and the cooling rate after deposition.

The thickness of the deposited layer depends on several factors, such as the distance between the sprayer and the substrate, substrate temperature, precursor solution concentration, and deposited precursor volume.

The effects of four variables (type of glaze, application temperature, precursor concentration, and deposited oxide) on the change in glaze appearance (colour and gloss) were analysed to evaluate the decorative possibilities of the technique.

2. EXPERIMENTAL PROCEDURE

2.1. PREPARATION AND CHARACTERISATION OF THE SUBSTRATES

Three industrial frits with different melting points were selected: A (twice-fire), B (single-fire, red body), and C (single-fire, white body) to prepare the fired white glazes used as substrates and thus evaluate the effect of the thermal behaviour of the fired glaze on the deposited film.

The glaze compositions were prepared from a mixture with about 10% SnO_2 and 90% industrial frit, to which kaolin d'arvor, CMC, TPP, and water were added to obtain a slip with a solids content of 70% by weight. Grinding was performed in a fast laboratory mill with alumina balls.

The thermal behaviour of the three glazes was determined by hot stage microscopy (Misura 3, Expert System SpA, Italy), and the glass transition temperature was obtained by differential thermal analysis (TGA/SDTA 851^e, Mettler Toledo, Switzerland), conducted on test pieces that had been previously fired according to the cycle used to obtain the fired glazes.

The glaze slips were applied on a porous white body with a 0.8 cm gauge slide applicator. The 10 x 10 cm test pieces were fired at the temperature that had been determined as the optimum temperature for each fired glaze (930ºC, 1100ºC, and 1160ºC for glazes A, B, and C, respectively).

2.2. APPLICATION OF THE THIN FILMS

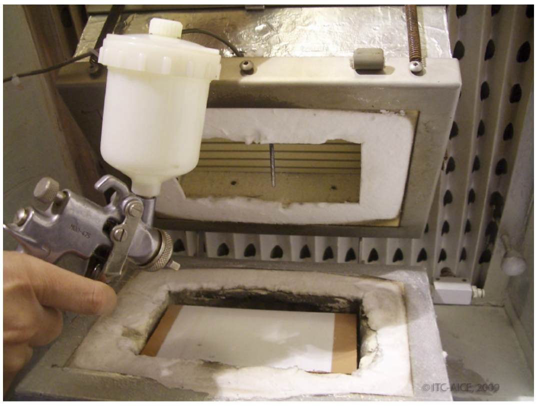

Figure 2. Airbrush application in the modified furnace.

Cobalt nitrate and copper nitrate solutions (1 M, 2 M, and 3M) were used as precursors for the films, proportioned by weighing and dispersed in the established quantity of water by magnetic stirring.

A specially designed electric laboratory furnace was used to heat the pieces to the selected application temperature for each experiment (400, 450, 500, or 550ºC). The furnace opened like a box, enabling the application to be performed on the piece inside the furnace, without needing to transfer the piece to a spray booth (Figure 2). After the application, the furnace was closed again in order to recover the initial temperature. When this was reached, the piece was withdrawn for rapid cooling.

2.3. CHARACTERISATION OF THE RESULTING SURFACES

The colour of the fired glazes was evaluated using two different instruments, depending on the optical characteristics of the applied coatings:

- A spectrophotometer with a geometry of 0º/8º for the coatings that displayed no special effects (Color-Eye 7000A, X-Rite, USA).
- A goniospectrophotometer according to standard DIN 6175-2 for the coatings that displayed a metallised appearance (GE742, X-Rite, USA). At a 45º angle of illumination, its optical configuration allows the spectral composition of the light returned by the sample at 4 aspecular observation angles (25º, 45º, 75º, and 110º) to be determined, the aspecular angle being the angle defined with respect to the direction specular to the illumination.

The gloss of the samples obtained was determined with a reflectometer (Statistical Novo-Gloss, Rhopoint, UK). Four gloss measurements were made on each test piece at a measurement angle of 60º.

The microstructure of the test pieces was analysed with a scanning electron microscope (Quanta 200F, FEI Co, USA). Surface analysis was performed with an EDX (Genesis 7000 SUTW, EDAX, USA) instrument.

3. RESULTS

3.1. CHARACTERISATION OF THE FIRED GLAZES

The characteristic temperatures of three glaze compositions are listed in Table 1. In the case of T_g, the transition was not very pronounced; the range in which the transformation took place was therefore defined, instead of a definite temperature. The results matched the expected outcome, a quite wide range being obtained with regard to the thermal behaviour of the three selected glazes. Of the six evaluated temperatures, only T_g overlapped to a certain extent with the range of the film deposition temperatures, so that this was the temperature that might exhibit some correlation with the results of the process, followed by the shrinkage start temperature. The other temperatures were already too high with respect to the operating range for film application.

Test	Characteristic temperature (ºC)	A	B	C
Hot stage microscope	Shrinkage start (T_{IC})	585	790	860
	Shrinkage end (T_{FC})	710	1000	1090
	Softening (T_R)	785	1030	1110
	Sphere (T_E)	855	1075	1150
	Half sphere ($T_{1/2}$)	950	1195	1250
	Melting (T_F)	1000	1225	1340
DTA	Transformation (T_g)	510-543	630-668	707-740

Table 1. Characteristic temperatures of the glazes used as substrates.

3.2. CHARACTERISATION OF THE FILMS OBTAINED FROM $Cu(NO_3)_2$

It was visually observed that the coated glaze substrates acquired a golden hue and notably higher gloss.

Although the chromatic coordinates of the fired glazes exhibited a certain scatter (Figures 3, 4, and 5), comparison of the averages values for each variable enabled the following effects to be identified:

- The substrate did not appear to have any definite effect on the resulting colour.
- An increase in precursor concentration tended to notably decrease the lightness and slightly decrease the yellow component, without any definite effect on the red component being noted.
- A rise in the operating temperature tended to increase the lightness of the colour, and to slightly decrease both the red and the yellow component.

Therefore, the brightest golden hue would be obtained with a low precursor concentration, operating at high temperature.

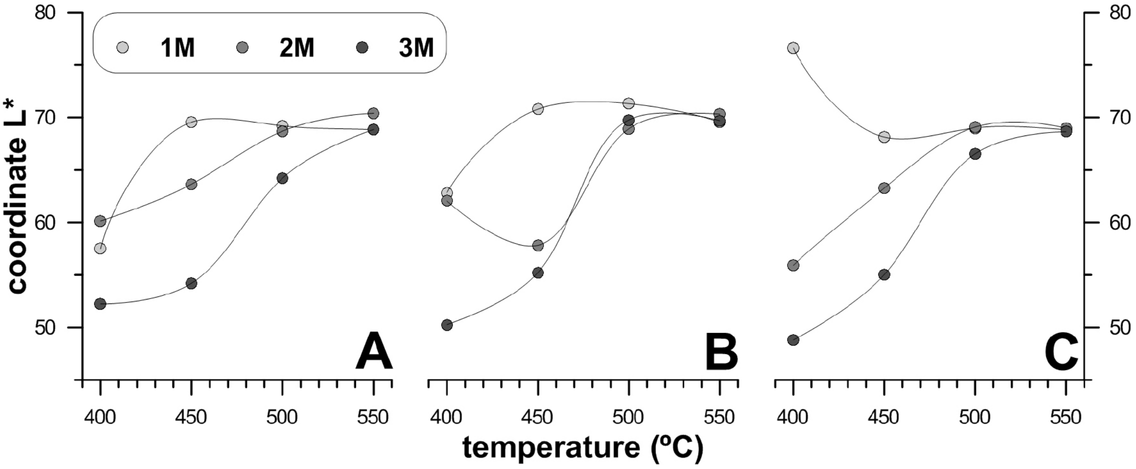

Figure 3. Evolution of the L coordinate of the samples as a function of the substrate, application temperature, and precursor concentration.*

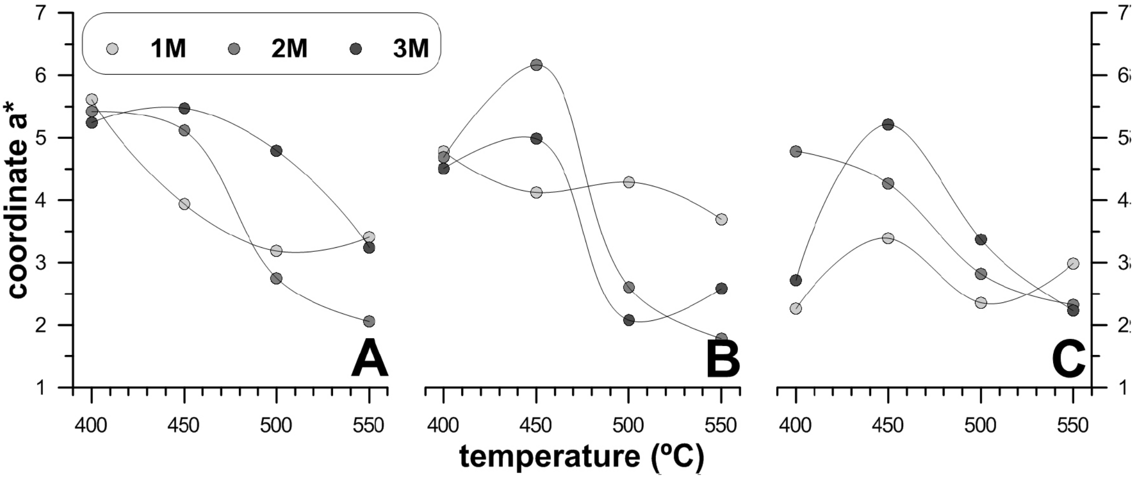

Figure 4. Evolution of the a coordinate of the samples as a function of the substrate, application temperature, and precursor concentration.*

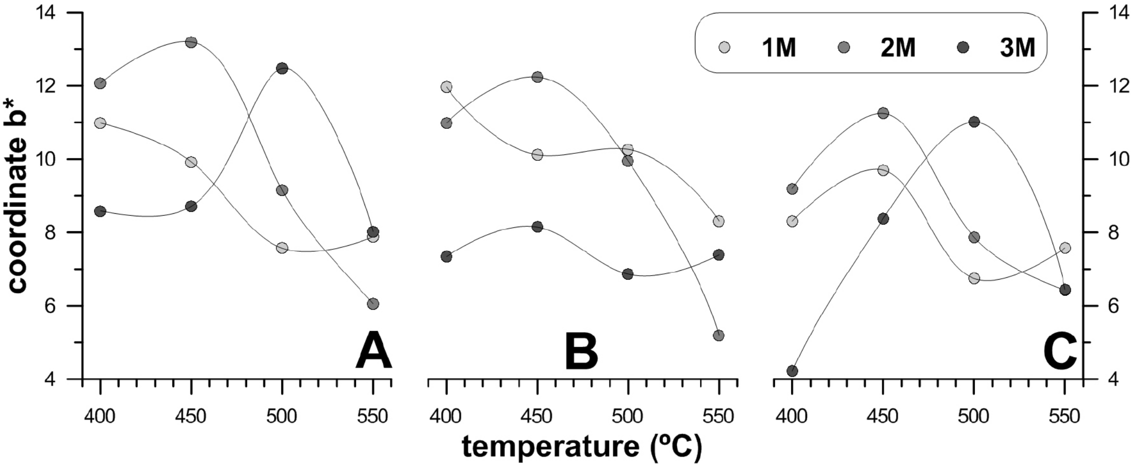

Figure 5. Evolution of the b coordinate of the samples as a function of the substrate, application temperature, and precursor concentration.*

Despite the notable change in colour, the most spectacular result was the increase in fired glaze gloss (Figure 6), which in certain cases tripled the value of the substrate (in the most extreme case reaching 318‰). In regard to this property, the effect of the studied variables was as follows:

- A slight effect of the fired glaze on the resulting gloss was detected: fired glaze B appeared the most prone to produce the highest values, whereas fired glaze C produced the lowest increase.
- The precursor concentration had a notable effect, the 2M concentration tending most to raise gloss.
- Gloss also depended on the operating temperature, it being advisable to operate at high temperatures (500ºC), albeit not at the bound of the explored range (550ºC).

The results indicated that, to obtain the highest gloss values, it was advisable to perform the application on fired glaze B, using an intermediate precursor concentration, operating at relatively high temperatures.

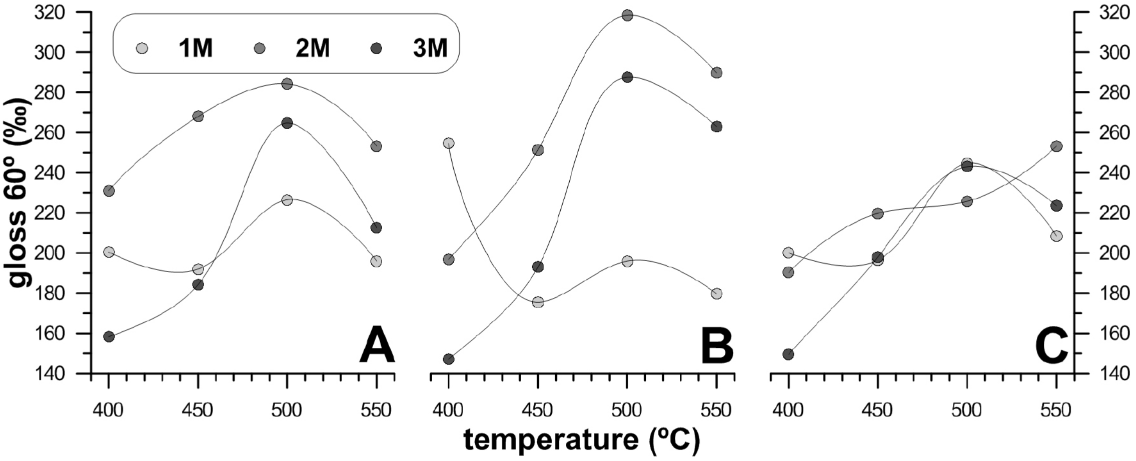

Figure 6. Evolution of gloss of the samples as a function of the substrate, application temperature, and precursor concentration.

In order to characterise the microstructure of the applied film, the sample with the highest gloss was chosen. The SEM images indicated that the applied film exhibited a homogeneous appearance and was made up of nanocrystals (between 20 and 70 nm). These were bonded together but did not form a compact sheet. Below the applied film, large acicular crystals of tin oxide were detected. Energy-dispersive X-ray (EDX) analysis showed that copper was present at the surface of the fired glaze. It was not possible to distinguish regions with greater or lesser concentrations of copper, which confirmed the homogeneity of the deposited film. The copper compound deposited on the surface could not be identified, though it was presumably CuO from nitrate decomposition.

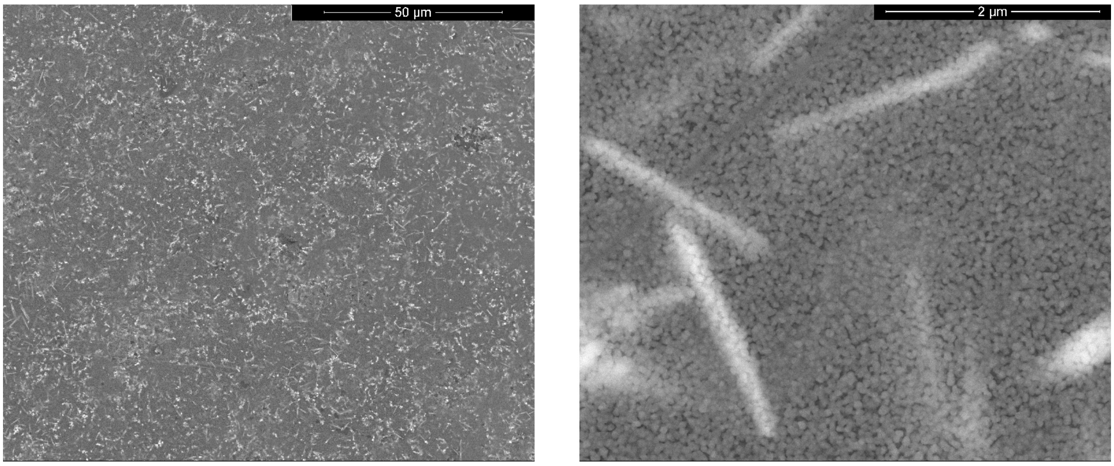

Figure 7. Surface of the sample obtained on applying the copper nitrate solution with a 3M concentration at 500ºC on fired glaze B.

3.3. CHARACTERISATION OF THE FILMS OBTAINED FROM $Co(NO_3)_2$

In the case of the cobalt precursor application, the surfaces acquired a greyish hue, developing quite dark surfaces in certain cases. However, unlike what occurred in the copper application, the appearance of a metallic effect on some of the pieces to which cobalt had been applied was visually observed. The fired glazes with a "metallised" appearance displayed variations in colour, depending on the observation angle, so that their appearance could not be properly evaluated with the diffuse reflectance spectrophotometers. This was because the chromatic coordinates that were evaluated with this equipment might have corresponded to colours far removed from those that were visually observed, particularly when the illumination–piece–observer angle was modified. In order to quantify this effect in some way, the "metallisation index" described in the literature[14] was used, which allows the "metallized" appearance of fired glazes to be instrumentally evaluated from the measurements of a goniospectrophotometer using four angles. This needs no external references and does not depend on the angle at which the greatest colour difference appears.

The metallisation index (I_M) was calculated from Eq. 1. According to the proposers of the I_M, an I_M above 5 indicates that a glaze has a "metallised" appearance.

$$I_M = \frac{\Delta E^*_{25-45} + \Delta E^*_{25-75} + \Delta E^*_{25-110} + \Delta E^*_{45-75} + \Delta E^*_{45-110} + \Delta E^*_{75-110}}{600 \cdot \sqrt{2/3}} .100 \qquad \text{Eq. 1}$$

The I_M values obtained displayed a scatter similar to that observed with the chromatic coordinates in the case of the copper coatings (Figure 8). However, analysis of the values, averaged by variables, indicated the following trends:

- The metallised effect was independent of the fired glaze used as substrate.
- The highest precursor concentrations favoured the appearance of the metallised effect.
- Operating at the lowest temperature in the range analysed slightly favoured the appearance of the metallised effect.

Consequently, in order to maximise this effect, it would be convenient to operate with the most concentrated precursor at the lowest operating temperature.

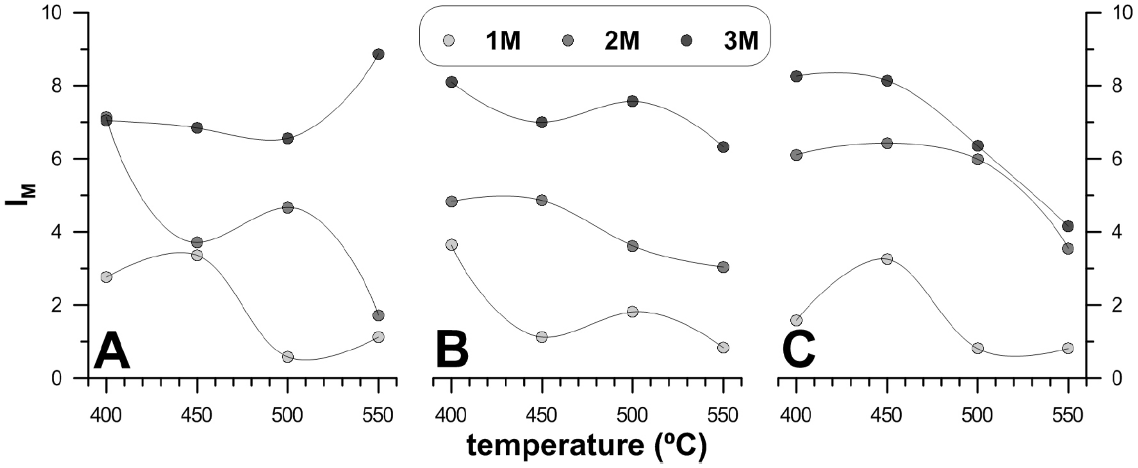

Figure 8. Evolution of the metallisation index of the samples as a function of the substrate, application temperature, and precursor concentration.

The application of cobalt did not lead to such spectacular development of the gloss as was the case with copper. Although a moderate increase in gloss was observed in most test pieces, in some cases the coated piece exhibited a lower gloss than the original substrate (Figure 9). Analysis of the average values identified the following trends:

- Substrate B was the most favourable for obtaining increased gloss, whereas substrate C was the least recommendable.
- The highest gloss values were obtained with the lowest precursor test concentration, whereas the highest concentrations tended to generate pieces with lower gloss than the original substrate.
- In order to obtain the highest gloss values, it would be convenient to operate at high temperature (500ºC), though not at the maximum temperature in the tested range (550ºC).

It was noted that the relationships of the gloss with the substrate and the operating temperature were similar to those found in the case of copper, and only the concentration behaved a little differently.

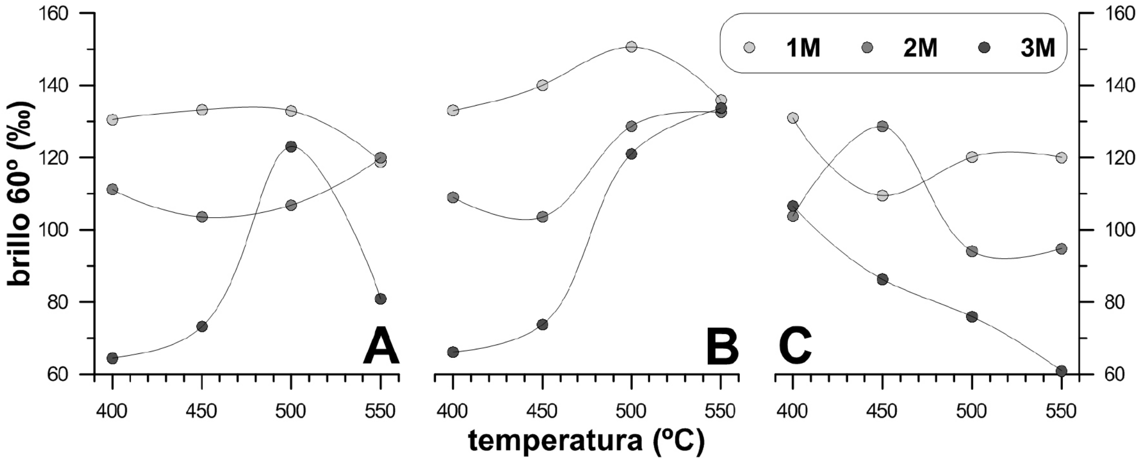

Figure 9. Evolution of gloss of the samples as a function of the substrate, application temperature, and precursor concentration.

The piece that had generated the greatest gloss in the series was chosen for the evaluation of its microstructure (Figure 10). The SEM images indicated that the surface of the fired glaze on which cobalt had been applied displayed spot build-ups of material, which were probably the drops produced in spraying. The microstructure was very similar to that of the copper application, though the nanocrystals appeared to be slightly larger.

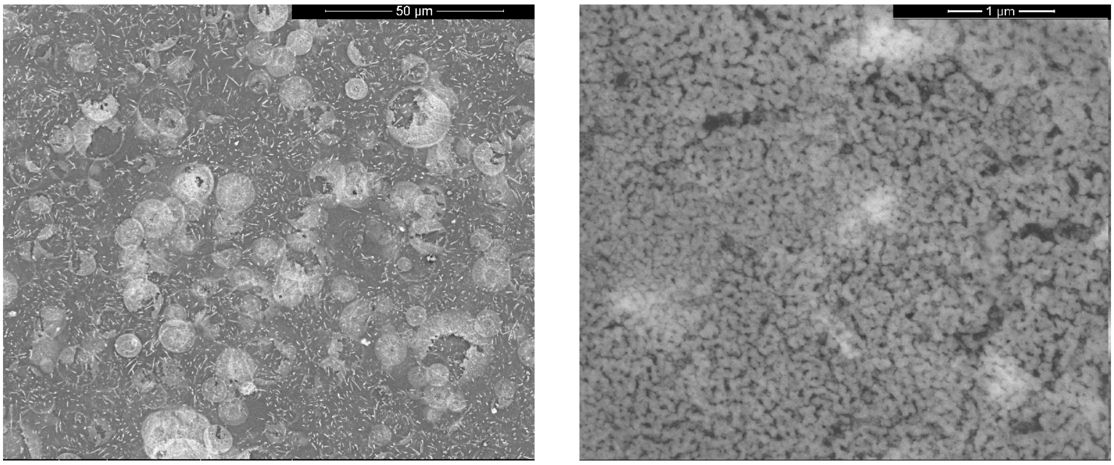

Figure 10. Surface of the sample obtained on applying the cobalt nitrate solution with a 1M concentration at 500ºC on fired glaze B.

The difference in gloss behaviour might be interpreted by the greater ease of the Co precursor to generate material build-ups on the surface of the fired glaze, which would reduce the end gloss of the surface. It would also be necessary to consider the differences in the optical properties of the deposited nanocrystals.

4. CONCLUSIONS

The study shows that spray pyrolysis enabled the surface appearance of fired glazes to be substantially modified by a method that can be readily implemented and requires no environmentally troublesome precursors.

The application of a copper nitrate solution in the appropriate conditions spectacularly increased the gloss of the treated surface, in addition to providing it with a golden hue. In the case of the cobalt nitrate, under appropriate conditions, a dark grey can be generated from a white substrate, which in addition displays a metallised appearance.

It was verified that the fired glaze used as substrate hardly affected the colour or metallised appearance of the end surface. However, it did influence the gloss, though no correlation was found with the characteristic temperatures of the fired glaze.

Depending on the sought-after end effect, the solution concentration and the operating temperature need to be judiciously chosen because they influence the colour, gloss, and metallised appearance.

The two studied precursors gave rise to a deposited film made up of nanocrystals that were bonded together, though they did not form a compact sheet. In the case of copper, the film was more even and the nanocrystals slightly smaller. In contrast, the cobalt tended to generate a more heterogeneous film (material build-ups were noted, possibly from the spray drops) and the nanocrystals were slightly larger.

5. ACKNOWLEDGEMENTS

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